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Donor–Acceptor Bonding. VI. The Reactions of Trimethylamine, Dimethylamine, Monomethylamine, and Ammonia with Titanium Tetrachloride and of Trimethylamine with Titanium Trichloride[1]

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The Me_3N–$TiCl_4$, Me_2NH–$TiCl_4$, $MeNH_2$–$TiCl_4$ and NH_3–$TiCl_4$ systems have been studied. Addition reactions were found to be complicated by ammonolytic cleavage when N–H links were present in the donor molecule and also by oxidation–reduction reactions. The ability of the methylamines and NH_3 to reduce titanium(IV) decreases as the number of methyl groups decrease, and in all cases increases as the temperature is raised. The addition compounds $Me_3N \cdot TiCl_4$ and $(Me_3N)_2 \cdot TiCl_3$ were isolated from the Me_3N–$TiCl_4$ adducts. The latter compound was prepared also in 100% yield by the direct reaction of Me_3N and $TiCl_3$. Both addition compounds are sublimable, crystalline solids of low thermal stability. The infrared absorption spectrum of $(Me_3N)_2 \cdot TiCl_3$ is closely related to that of Me_3N. Its magnetic susceptibility is near the theoretical value calculated for one unpaired electron per titanium atom. The thermal decompositions of all gross adducts and the purified addition compounds were studied. The adduct of NH_3 and $TiCl_4$, which had the empirical composition $(NH_3)_2 \cdot TiCl_4$ contained NH_4Cl. On heating to 160° the presence of reduced titanium was detected, indicating that the TiNCl reported as a product of the thermal decomposition of the system NH_3–$TiCl_4$ may not be a compound of tetravalent titanium. Possible reaction mechanisms and the structures of titanium halide molecular addition compounds are discussed.

Introduction

Titanium tetrachloride has long been known to complex with electron pair donor molecules. However, only a few of its addition reactions have been critically studied, and this is particularly true of the systems involving nitrogen donors. In contrast, the acceptor properties of $TiCl_3$ are almost unknown.[3]

The reactions of $TiCl_4$ with NH_3 have been investigated by numerous workers,[4] and the formation of various amidochlorides, *e.g.*, $Ti(NH_2)_3Cl$, has been shown[4m] to be characteristic of this system. Thermal decomposition *in vacuo* of NH_3–$TiCl_4$ adducts yields a solid of the formula TiNCl.

The tendency of $TiCl_4$ to participate in oxidation–reduction reactions with certain organic systems has generally not been recognized, and it seemed desirable to consider this possibility with a series of related bases, the methylamines and NH_3. Ammonolytic cleavage could be expected to be a complicating feature of the addition reactions with the donor molecules containing N–H links.

Experimental

Materials and Manipulation.—Eimer and Amend C.P. $TiCl_4$ was refluxed over mercury and distilled in an all glass system. Moisture was excluded by a P_2O_5 drying tube. Anhydrous $TiCl_3$ was prepared by reducing $TiCl_4$ with hydrogen[3] (Calcd.: Ti, 31.05; Cl, 68.95. Found: Ti, 32.1; Cl, 68.0; reducing power, 99.2%, by titration with standard $Fe_2(SO_4)_3$ to the red end-point of the iron thiocyanate complex). The Matheson tank Me_3N used in the direct reaction with $TiCl_3$ was dried and freed of impurities containing labile hydrogen by treatment with freshly sublimed, ground P_2O_5.[5] Matheson amines and NH_3 used in all the reactions with $TiCl_4$ were dried by passage through porous BaO.[6] All manipulation of the solid adducts between the titanium halides and nitrogen bases was in a nitrogen atmosphere using a small, tight metal dry box. It was necessary to pay particular attention to assure complete removal of moisture because of the extreme tendency of the adducts to absorb water, with subsequent decomposition. After loading, the box interior was flushed for a long time with oil pumped nitrogen, and then residual water was condensed on the cold surface of a glass bulb which could be filled with liquid nitrogen through connections to the outside.

I. **The System** Me_3N–$TiCl_3$. **Preparation of** $(Me_3N)_2 \cdot TiCl_3$.—Bis-trimethylamine titanium trichloride, $(Me_3N)_2 \cdot TiCl_3$, was prepared by the direct reaction of $TiCl_3$ with excess amine. Crystals of $TiCl_3$ were ground to a fine powder in the dry box and transferred to the reaction vessel. The vessel was evacuated and Me_3N condensed at −78° onto the $TiCl_3$. The system was warmed to *ca.* −5° and the suspension in liquid amine churned continuously with a glass-enclosed magnetic stirrer. After several hours, when reaction appeared complete, as evidenced by no further color change of the solids, excess amine was pumped completely from the system. The X-ray powder diffraction pattern of the blue-green crystalline solid showed none of the lines characteristic of $TiCl_3$. $(Me_3N)_2 \cdot TiCl_3$ can be recrystallized from liquid Me_3N.

Analyses.—Samples were loaded into tared glass tubes in the dry box, sealed, and weighed. Analyses for titanium and chlorine were made gravimetrically on the same sample, the titanium by precipitation of hydrous titanic oxide from a dilute HNO_3 solution followed by ignition to TiO_2, and chlorine by precipitation of AgCl from the filtrate. Carbon and hydrogen were determined by the conventional microcombustion technique. Analyses for nitrogen by the micro Dumas method were erratic. Similar difficulty was encountered with the adducts of the methylamines and $TiCl_4$.[7]

Anal. Calcd. for $(Me_3N)_2 \cdot TiCl_3$: Ti, 17.58; Cl, 39.04; C, 26.44; H, 6.66. Found: Ti, 17.76; Cl, 38.77; C, 26.51; H, 6.63.

Attempts to titrate the Ti(III) of $(Me_3N)_2 \cdot TiCl_3$ dissolved in water, dilute HCl, or dilute H_2SO_4 were made directly with standard $Fe_2(SO_4)_3$, $K_2Cr_2O_7$, and indirectly by the titration with $K_2Cr_2O_7$ of the Fe(II) produced by the addition of excess $Fe_2(SO_4)_3$. Low, highly erratic results were always obtained. Aqueous solutions of the addition compound were usually slightly cloudy.

Volatility and Thermal Stability.—$(Me_3N)_2 \cdot TiCl_3$ can be slowly sublimed *in vacuo* at moderate temperatures, *e.g.*, with a temperature differential from 20 to 5°. At higher

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(1) Presented before the Division of Physical and Inorganic Chemistry of the American Chemical Society, Chicago, Ill., September, 1953. Paper V of this series, A. W. Laubengayer and Wm. C. Smith, THIS JOURNAL, **76**, 5985 (1954).

(2) Abstracted from the thesis submitted to the Graduate School, Cornell University, June 1953, by Morton Antler in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(3) Di- and hexammines of $TiCl_3$ have been reported by W. C. Schumb and R. F. Sundström, THIS JOURNAL, **55**, 596 (1933).

(4) (a) H. Rose, *Pogg. Ann.*, **16**, 57 (1829); (b) H. Rose, *ibid.*, **24**, 141 (1832); (c) J. Persoz, *Ann. Chem. Phys.*, [2] **44**, 321 (1830); (d) A. Rosenheim and O. Schütte, *Z. anorg. Chem.*, **26**, 239 (1901); (e) M. Blix and W. Wirbelauer, *Ber.*, **36**, 4228 (1903); (f) A. Stahler, *ibid.*, **38**, 2619 (1905); (g) N. Whitehouse, *J. Soc. Chem. Ind.*, **26**, 738 (1907); (h) O. Ruff and F. Eisner, *Ber.*, **41**, 2250 (1908); (i) L. Denis-Nathan, Ph.D. Thesis, U. of Capetown, S. A., 1929; (j) A. Brager, *Acta Physicochim. U.R.S.S.*, **10**, 887 (1939); (k) C. M. Olson, U. S. Patent 2,413,778 (1947); (l) F. J. Sowa, U. S. Patent 2,606,815 (1952); (m) G. W. A. Fowles and F. H. Pollard, *J. Chem. Soc.*, 2588 (1953).

(5) P. D. Ingram, M.S. Thesis, The University of Chicago, 1940.

(6) Obtained from Barium and Chemicals, Inc., Willoughby, Ohio.

(7) A. Steyermark, "Quantitative Organic Microanalysis," The Blakiston Co., New York, N. Y., 1951, pp. 56, 134, 135.

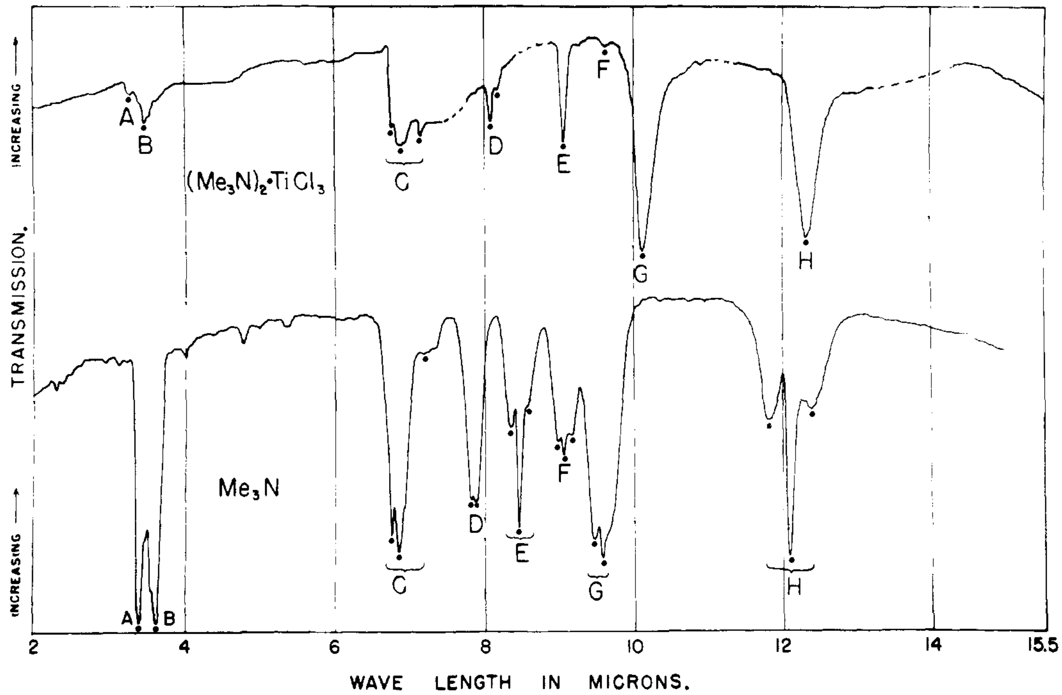

Fig. 1.—Infrared spectra of solid $(Me_3N)_2TiCl_3$ and gaseous Me_3N. Analogous absorption maxima of the compounds indicated by the same letter.

charge temperatures, *e.g.*, 75°, marked decomposition takes place with the formation of unsublimable, non-hygroscopic solids containing much Ti(III), chlorine and Me_3N which can be recovered by the addition of aqueous alkali. The addition compound is stable at room temperature in a nitrogen atmosphere or *in vacuo*.

X-Ray Diffraction Pattern and Density.—The powder X-ray diffraction pattern of $(Me_3N)_2 \cdot TiCl_3$ was obtained with Cu Kα radiation using a nickel filter. The *d* spacings are listed in Table I, along with visually estimated intensities on a scale of vs to vw, very strong to very weak.

Table I

Powder X-Ray Diffraction Patterns

$(Me_3N)_2 \cdot TiCl_3$				$Me_3N \cdot TiCl_4$	
d	Estimated intensity	*d*	Estimated intensity	*d*	Estimated intensity
6.73	w	2.66	m	6.15	w
6.15	vs	2.55	w	5.53	vs
5.47	vw	2.41	m	4.82	s
5.09	m	2.33	m	4.43	vw
4.87	w	2.06	vw	3.93	m
4.22	m	1.97	m	2.97	m
3.99	m	1.86	vw	1.52	vw
3.70	s	1.82	vw		
3.55	m	1.76	w		
3.27	w	1.72	w		
3.14	s	1.55	vw		
2.95	s	1.47	vw		
2.79	m	1.41	vw		

The density of $(Me_3N)_2 \cdot TiCl_3$, determined by the displacement of Nujol, in which it is insoluble, is 1.33 g./cm.^{3} at 25°.

Infrared Spectrum.—The infrared absorption spectra of solid $(Me_3N)_2 \cdot TiCl_3$ and of gaseous Me_3N, in the region 2 to 15 μ, are shown in Fig. 1. The spectrum of $(Me_3N)_2 \cdot TiCl_3$ is a composite of several spectra obtained by eliminating the characteristic peaks of the Nujol and halocarbon mulling oils. The addition compound has maxima at 3.26, 3.47, 6.77, 6.90, 7.16, 8.08, 8.16, 9.06, 9.60, 10.12 and 12.30 μ. Titanium trichloride does not absorb in this region. The spectrum of $(Me_3N)_2 \cdot TiCl_3$ resembles that of Me_3N. If one assumes that absorptions due to the Ti–N and Ti–Cl bonds appear only at lower frequencies, correlation of the maxima of free Me_3N with those of the modified amine unit in the addition compound becomes possible; the same letters in Fig. 1 applied to both spectra refer to what are presumed to be analogous absorption maxima. The displacements may be interpreted to indicate a lengthening of the C–N separations and a shortening of the C–H bonds of Me_3N as a consequence of condensation and complex formation.

Magnetic Susceptibility.—The gram molar susceptibility of $(Me_3N)_2 \cdot TiCl_3$ at 20°, measured by the Gouy method,[8] is $1019 \pm 34 \times 10^{-6}$. If one estimates the diamagnetic contribution of the molecule to be -180×10^{-6} and assumes that the Curie law is obeyed, the effective Bohr magneton number of Ti(III) calculates to 1.68 ± 0.03. This is close to the theoretical value of 1.73 for one unpaired electron when the orbital moment is quenched, the magnetic moment arising from spin only. No paramagnetic resonance absorption was found at 20° or at −196°.

II. The System Me_3N–$TiCl_4$. Method of Reaction and Analyses.—Trimethylamine and gaseous $TiCl_4$, highly diluted by nitrogen, were mixed at room temperature in the wide range of mole ratios given in Table II. Dry nitrogen was bubbled through $TiCl_4$ and the vapor mixture was introduced into a flask simultaneously with Me_3N. Excess reactant and nitrogen passed out of the vessel. The colored, finely divided solid adducts listed in Table II collected on the walls of the flask. The empirical mole ratios of Me_3N to $TiCl_4$ combined in these adducts were determined by analyses for titanium, chlorine, carbon and hydrogen.

Table II

Reaction Conditions and Analyses of Adducts of Me_3N and $TiCl_4$

Mole ratio of $Me_3N/TiCl_4$		
In reaction mixture used	In adduct formed	Color of solid adduct
1/10	1.3/1	Yellow-brown
1/1		Yellow
5/1		Yellow-green
15/1	2.7/1	Orange-red

Only an analytically insignificant amount of Me_3N could be pumped from the adducts, indicating that little amine

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(8) P. W. Selwood, "Magnetochemistry," Interscience Publishers, Inc., New York, N. Y., 1943, pp. 2–6.

was retained by adsorption. Powder X-ray diffraction patterns of the 1.3/1 and 2.7/1 products were different but too diffuse to allow certain identification of any constituent.

The presence of Ti(III) in all adducts was confirmed by their ability to reduce aqueous solutions of common oxidizing agents such as methylene blue and ferric salts and by the precipitation, on the addition of alkali, of blue-black $Ti_2O \cdot nH_2O$ which turned white on exposure to air. Possible interferences with these tests were checked using known solutions of $TiCl_3$ and NH_4^+ or Me_3NH^+ salts; acidic solutions containing only Ti(IV), Cl^- and NH_4^+ or Me_3NH^+ gave no positive tests.

The vapor phase preparation of an adduct at −5° using a $Me_3N/TiCl_4$ mole ratio slightly greater than one gave a yellow adduct that analyzed to the ratio 1.2/1. The test for Ti(III) was positive but much weaker than for the adducts prepared at room temperature.[9]

There was no increase in the reducing power of any $Me_3N-TiCl_4$ adduct on standing for several weeks at room temperature. After heating to 100° for 3 minutes, all adducts gave much stronger Ti(III) tests.

Attempts made with a large number of anhydrous organic solvents failed to extract a pure titanium compound from a product prepared with $TiCl_4$ in excess in the reaction vessel. In most cases, *e.g.*, with ligroin, benzene, carbon tetrachloride, ethyl ether and nitrobenzene, solubility was negligible. Solution of the adduct, accompanied by vigorous reaction, was complete with dimethylformamide.

Sublimation Experiments. Isolation of $Me_3N-TiCl_4$.—The product of a preparative run, made with $TiCl_4$ in excess, was heated in a semi-micro vacuum sublimator.[10] Five grams of adduct held for several weeks at 20° with the collecting surface at 5° gave a first fraction of 0.7 g. of a mixture of yellow crystals and blue-green crystals. Further sublimation of the residue at 140° yielded a solid fraction identified as Me_3NHCl. Heating the residue was resumed, and a clear, colorless liquid, unidentified but free of titanium, appeared at 150°. The sizeable residue after heating to 195° was a water-soluble, brown-black solid that gave very strong Ti(III) and chlorine tests, and evolved Me_3N on the addition of aqueous alkali.

The adducts of many preparative runs in which $TiCl_4$ was introduced in excess were sublimed, and the nature of the first fraction obtained by sublimation at room temperature varied from adduct to adduct. Often the sublimate consisted only of blue-green, crystalline $(Me_3N)_2 \cdot TiCl_3$, identified by chemical analysis and its powder X-ray diffraction pattern. Other adducts gave $(Me_3N)_2 \cdot TiCl_3$ in admixture with yellow crystals, and the relative amounts of the two substances varied considerably. A sublimate that consisted entirely of the yellow compound was never obtained. It was not possible to separate the two compounds by fractional sublimation because of their almost identical volatility. Accordingly, identification of the yellow substance was based on qualitative studies of a few small single crystals separated by hand in the dry box, and on analysis of a mixture of the two compounds.

Only titanium(IV), chlorine and Me_3N were found in the yellow crystals. Quantitative determinations were made on a mixed sublimate that consisted predominantly of yellow crystals (proven by microscopic examination and the powder X-ray diffraction pattern of the mixture).

Anal. Found: Ti, 19.6; Cl, 55.3; C, 16.5; H, 4.1. Calcd. for a mixture of 90% of $Me_3N \cdot TiCl_4$ and 10% of $(Me_3N)_2 \cdot TiCl_3$: Ti, 19.1; Cl, 55.2; C, 15.6; H, 4.0.

An evaluation of the reliability of the analytical procedures and a consideration of all possible compositions of the mixture indicated that the yellow crystals could be only $Me_3N \cdot TiCl_4$. Separate evidence of the existence of this compound was obtained in the initial preparative work, for the gross composition of the adducts approached 1/1 when the reaction temperature was lowered and the amount of Ti(III) formed was reduced. $Me_3N \cdot TiCl_4$ is extremely hygroscopic, and in this work was handled only in a nitrogen atmosphere in the dry box.

The powder X-ray diffraction pattern of $Me_3N \cdot TiCl_4$, obtained with Cu Kα radiation using a nickel filter, is listed in Table I.

Thermal Stability of $Me_3N \cdot TiCl_4$.—A few individual crystals of $Me_3N \cdot TiCl_4$ heated in a vacuum sublimator at 55° resublimed in part. The considerable tan residue that remained tested positively for Ti(III), chlorine and volatile base. There was no indication that $(Me_3N)_2 \cdot TiCl_3$ is a product of the thermal decomposition of $Me_3N \cdot TiCl_4$. The quantity of $Me_3N \cdot TiCl_4$ available was very small, however, and traces of sublimable decomposition product may have escaped detection.

$Me_3N \cdot TiCl_4$ is not stable *in vacuo* at room temperature. Thermal decomposition is slow, but in two or three months crystals show marked dulling and loss of transparency. Under the same conditions of storage, $(Me_3N)_2 \cdot TiCl_3$ is unchanged.

III. The System $Me_2NH-TiCl_4$ and $MeNH_2-TiCl_4$.—Vapor phase reactions at room temperature with an excess of $TiCl_4$ gave hygroscopic, colored, finely divided solid products. The dimethylamine adduct was mottled, containing orange, yellow, green, and grey particles in admixture, while the more homogeneous monomethylamine adduct was orange-red.

Anal. Dimethylamine adduct, found: Ti, 14.85; Cl, 42.96; C, 20.55; H, 6.75. Calcd. for $(Me_2NH)_3 \cdot TiCl_4$: Ti, 14.74; Cl, 43.64; C, 22.17; H, 6.51.

Monomethylamine adduct, found: Ti, 15.48; Cl, 44.72; C, 14.75; H, 6.6; Calcd. for $(MeNH_2)_4 \cdot TiCl_4$: Ti, 15.26; Cl, 45.17; C, 15.30; H, 6.42.

Qualitative tests for Ti(III) on the adducts, carried out in a nitrogen atmosphere, were weakly positive with $Me_2NH-TiCl_4$ and negative with $MeNH_2-TiCl_4$. The amines could be volatilized from aqueous solutions of the adducts on the addition of alkali.

The thermal decomposition of both adducts was examined to 200° in the vacuum sublimator. Sublimable amine hydrochloride and unidentified volatile liquids were obtained, but none of the condensates contained titanium. The residues were completely soluble in water and gave very strong positive tests for Ti(III), chlorine and volatile base.

There was no solubility of either adduct in the common anhydrous organic solvents used in analogous work with the $Me_3N-TiCl_4$ adduct, but again there was reaction with and complete solution in dimethylformamide.

IV. The System NH_3-TiCl_4.—The vapor phase reaction of NH_3 and $TiCl_4$ was carried out at room temperature in the same manner as in the amine–$TiCl_4$ work, with $TiCl_4$ held in slight excess over the mole ratio of 2/1. This limitation of the quantity of NH_3 available for complexing differs from the approach of previous workers who invariably used an excess of the base. Thus, in our work the conditions were not favorable for severe ammonolytic decomposition.

A finely divided, hygroscopic yellow adduct was obtained and analyzed. The nitrogen determination was by the micro Dumas method.

Anal. Calcd. for $(NH_3)_2 \cdot TiCl_4$: Ti, 21.40; Cl, 63.38; N, 12.52; H, 2.70. Found: Ti, 22.26; Cl, 63.11; N, 12.45; H, 2.47.

Qualitative tests for Ti(III) on aqueous solutions of the adduct were negative. The powder X-ray diffraction pattern showed the presence of NH_4Cl.

Portions of this adduct were heated in sealed glass tubes in a nitrogen atmosphere. After 1.5 hours at 160° the adduct darkened to pale orange. Another sample at 200° for 1 hour turned orange-green. Positive tests for Ti(III) were obtained in a nitrogen atmosphere with aqueous solutions of both heated adducts.

Discussion

The reaction product between NH_3 and $TiCl_4$ obtained in this work is lower in NH_3 content than the initially formed adducts prepared by a variety of methods by other workers.[11] Conditions were chosen so that ammonolytic cleavage would not be favored, a very dilute reagent concentration and an excess of $TiCl_4$ being used. Nevertheless, NH_4Cl was detected as a reaction product. Since the ex-

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(9) R. C. Osthoff and J. Thruner condensed small measured amounts of Me_3N in increments on a known weight of $TiCl_4$ at −78° and measured the residual pressure at room temperature after each addition. A plot of the $Me_3N/TiCl_4$ mole ratio against pressure gave two straight lines which intersected at the ratio of 1/1 (private communication).

(10) L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., New York, N. Y., 1941, 2nd ed., Pt. II, p. 299.

(11) Fowles and Pollard[4m] made a 2/1 complex of NH_3 and $TiCl_4$ by heating adducts of higher NH_3 content to 180° *in vacuo*.

istence of an ammoniate of $TiCl_4$ has never been conclusively demonstrated, it is likely that the equation

$$TiCl_4(g) + 2NH_3(g) \longrightarrow Ti(NH_2)Cl_3(s) + NH_4Cl(s)$$

is correct, and this is in agreement with Fowles and Pollard's reasoning about the composition of the 2/1 adduct in NH_3 and $TiCl_4$ based on other evidence.

The presence of Ti(III) in aqueous solutions of the NH_3–$TiCl_4$ adduct which has been heated to only 160° suggests that TiNCl, prepared by heating NH_3–$TiCl_4$ adducts to much higher temperatures (270–300°, Ruff and Eisner; 270°, Denis-Nathan; 350–400°, Brager; 350°, Fowles and Pollard), may likewise contain Ti(III).[12] Indeed, Ruff and Eisner who first prepared TiNCl and TiNBr observed that aqueous NH_3 did not dissolve TiNBr, but that a blue coloration which disappeared quickly was produced. This constitutes a qualitative test for Ti(III).[13] There is considerable doubt as to the chemical individuality of TiNX materials. Brager's α-$(NH_3)_4TiCl_4$, obtained on heating an NH_3–$TiCl_4$ adduct to 200°, may have contained Ti(III).

The primary reaction between Me_3N and $TiCl_4$ below room temperature is simple addition to give $Me_3N{\cdot}TiCl_4$, in contrast to the ammonolytic reactions of NH_3 and $TiCl_4$. However, the mechanisms of the thermally very sensitive oxidation–reduction side effects can only be conjectured from available evidence. Two mechanisms appear possible: (1) It can be supposed that $TiCl_4$ may have chlorinated Me_3N to give CH_3–$N(CH_3)CH_2Cl$ or more highly chlorinated amine derivatives and that HCl and $TiCl_3$ were formed simultaneously. The HCl might then have combined with the CH_3–$N(CH_3)$-CH_2Cl to give a salt or with additional Me_3N giving Me_3NHCl. The various chlorinated amine products could have combined with additional Me_3N introduced into the system to produce quaternary ammonium salts. The $TiCl_3$ perhaps combined with Me_3N to give $(Me_3N)_2{\cdot}TiCl_3$. (2) Alternatively, if the formation of free radicals like CH_3–$N(CH_3)CH_2{\cdot}$ from Me_3N was involved (by loss of hydrogen atoms which, as above, might have produced intermediate $TiCl_3$ and HCl), dimers or high molecular weight organic polymers could form. Some of the HCl or $TiCl_3$ produced might have added to the basic nitrogen atoms to give hydrochloride salts or high molecular weight addition compounds besides $(Me_3N)_2{\cdot}TiCl_3$. If the reaction possibilities are as complicated as has been suggested, it is not difficult to see why such indefinite amounts of amine, from 1.3 to 2.7 or more moles of Me_3N per mole of $TiCl_4$, were found to react at room temperature, dependent on reaction conditions.

The Me_2NH–$TiCl_4$ and $MeNH_2$–$TiCl_4$ systems can be thought to be intermediate in complexity to the systems involving Me_3N and NH_3. The ready cleavage of HCl when N–H links are present, as demonstrated in the NH_3–$TiCl_4$ system, suggests that the adducts contained little or no molecular addition compound, but consisted largely of the respective amine hydrochloride and substituted titanium amidochlorides. Furthermore, the presence of the methyl groups complicated the initial reactions and the thermal degradations because of oxidation–reduction side reactions, probably analogous to those which take place in the Me_3N–$TiCl_4$ system. The number of N–Me links is an important factor in such oxidation–reductions, for the order of reducing ability of the amines[14] and NH_3 to $TiCl_4$ is $NH_3 < MeNH_2 < Me_2NH < Me_3N$.

The coördination numbers of 4 and 6 seem to be favored by titanium, at least in those structures which have been determined such as $TiCl_4$ and Rb_2TiCl_6. The tetrahedral and octahedral configurations of $TiCl_4$ and $TiCl_6^=$ are in line with those of analogous systems such as $SnCl_4$ and $SnCl_6^=$. However, many 1:1 molecular addition compounds of $TiCl_4$ have been reported previously; this fact and the empirical formulas of $(Me_3N)_2{\cdot}TiCl_3$ and $Me_3N{\cdot}TiCl_4$ obtained in the present work suggest that titanium may be able to achieve 5-coördination though it has not yet been demonstrated for any titanium compound. Another possibility is that the solids formed may actually be dititanium complexes with titanium having the favored coördination number of six, such as has been postulated for corresponding adducts of $SnCl_4$.[1] The low volatility of $Me_3N{\cdot}TiCl_4$ and $(Me_3N)_2{\cdot}TiCl_3$ would not be inconsistent with the existence of dititanium complex molecules in the vapor state. Structural analyses of molecular addition compounds involving titanium are needed.

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[12] N. V. Sidgwick, "The Chemical Elements and Their Compounds," Vol. I, Oxford, Clarendon Press, 1950, p. 640, has formulated this and the analogous bromine compound as N≡Ti–Cl and N≡TiBr, representations which involve tetravalent titanium.

[13] On the other hand, Fowles and Pollard found no paramagnetic behavior for TiNCl.

[14] It is likely that oxidation–reduction reactions in the systems of amines and $TiCl_4$ are common. W. R. Trost, *Can. J. Chem.*, **30**, 835, 842 (1952), has observed the reduction of $TiCl_4$ by $(C_2H_5)_3N$.